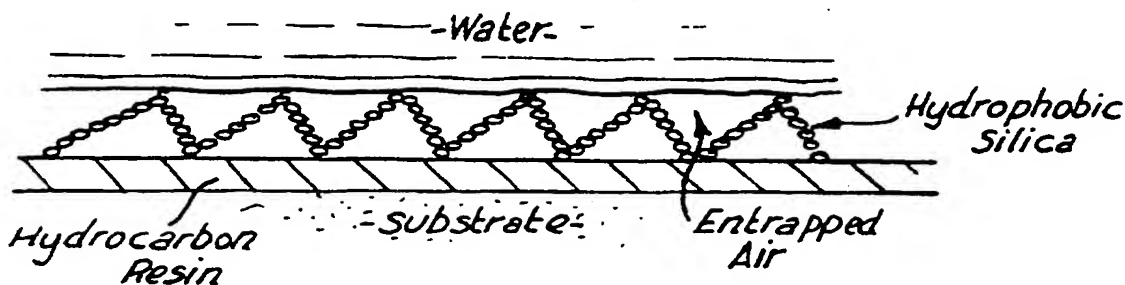




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C09D 5/16, B63B 1/38	A1	(11) International Publication Number: WO 97/29157 (43) International Publication Date: 14 August 1997 (14.08.97)
(21) International Application Number: PCT/GB97/00349 (22) International Filing Date: 7 February 1997 (07.02.97) (30) Priority Data: 9602602.6 7 February 1996 (07.02.96) GB 9618707.5 7 September 1996 (07.09.96) GB (71) Applicant (for all designated States except US): PROTECTIVE RESEARCH INDUSTRIES LIMITED [GB/GB]; Units 3A-3B, East Shawhead Industrial Estate, Coatbridge ML5 4LY (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): STARK, Ian, Strachan [GB/GB]; 2 Scotland Street Lane West, Edinburgh EH3 6PT (GB). FREW, Jeremy, George, McKenzie [GB/GB]; 109/2 Stenhouse Drive, Edinburgh EH11 3NW (GB). (74) Agent: MURGITROYD & COMPANY; 373 Scotland Street, Glasgow G5 8QA (GB).	(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	

(54) Title: COATING FORMULATION



(57) Abstract

A coating formulation or surface modification for use on or in respect of substrates, particularly those used in aqueous or fluid environments, produces and/or entraps a microlayer or gas or vapour at the interface between the substrate and the aqueous or fluid environment.

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1 "COATING FORMULATION"

2

3 The present invention relates to a coating or a surface
4 modification for substrates used in aqueous or fluid
5 environments such as sub-sea structures. More
6 particularly, the invention relates to a coating or
7 surface modification which can control the physical and
8 chemical properties of various substrates in contact
9 with aqueous or fluid environments.

10

11 Several problems are encountered in the use of
12 substrates in contact with aqueous or fluid
13 environments, and in particular in substrates used in
14 sub-sea structures.

15

16 Particular problems include growth of marine or other
17 fouling organisms such as algae, plant life or
18 crustaceans on the substrate and thus the creation of a
19 bio-net environment over the substrate.

20

21 Other problems are associated with the loss in energy
22 from the fluid flow over a given substrate due to
23 hydrodynamic drag coefficient properties intrinsic to
24 the individual fluid flow/substrate interface.

25

1 These factors affect the hydrodynamic drag coefficient
2 properties of fluid over the substrate, for example,
3 altering the hydro-dynamic properties of the substrate
4 in an aqueous system. Also, they can affect the water
5 repellent properties of the substrate and other
6 chemical and/or physical properties such as corrosion
7 resistance, thermal stability and structural
8 properties.

9
10 Attempts have been made to control fouling.
11 Traditional anti-fouling techniques have involved the
12 use of toxic materials to kill any organisms which grow
13 or are deposited onto the substrate. Typical materials
14 used are biocides, fungicides, Tri-butyl tin, Cuprous
15 Oxide, Antimony Oxide, Molybdenum Disulphide and lead
16 complexes. These are commonly known as leaching
17 processes. However, such materials have a severe
18 ecological impact.

19
20 Hydro-dynamic properties of substrates are
21 traditionally controlled in a number of ways. For
22 example, self polishing coatings are known which are
23 formulated to wear away or erode with time and friction
24 to keep the surface at an acceptable level of
25 hydrodynamic drag co-efficient.

26
27 Coatings may be formulated with an inclusion of
28 defrictionizing aids such as silanes, teflon and
29 Shell's Epikote-Coal Tar resin systems which are
30 commercially available.

31
32 Also, water repellent properties can be improved by
33 incorporating waxes, silanes, siloxanes, silicon
34 molecules and modified resins into the substrate.

35
36 Corrosion resistance is traditionally achieved using

1 techniques such as corrosion resistant resins (i.e.
2 epoxy, vinyl ester etc), zinc rich sacrificial primers,
3 phosphorus and chromate derivatives and toxic acid
4 within the substrate.

5
6 Each of these approaches aims to improve the chemical
7 and/or physical properties of a substrate, in terms of
8 corrosion resistance, thermostability and structural
9 properties but do not take into effect the ecological
10 impact on the marine environment. Prevention and
11 control of the formation of a bio-net is usually
12 attained by the use of toxic materials.

13
14 It is an object of the present invention to provide a
15 coating formulation or surface modification for use on
16 or in respect of substrates to be placed in an aqueous
17 or fluid environment whereby the properties of the
18 substrate which make it suitable for use in this
19 environment are maintained or improved with negligible
20 ecological impact.

21
22 According to the present invention there is provided a
23 formulation suitable for coating or modifying the
24 surface of a substrate to be situated in an aqueous or
25 fluid environment wherein the formulation is capable of
26 producing and/or entrapping a micro layer of gas or
27 vapour phase between the substrate and the aqueous or
28 fluid environment.

29
30 Optionally the entrapped gas may be air.

31
32 Preferably, the formulation comprises of a structure of
33 micro-particles, semi or semi-permeable foams or
34 membrane, micro-filaments or combinations of any or all
35 or the above which entrap the gas or vapour between the
36 aqueous or fluid environment and the substrate. In

1 aqueous systems the structure is preferably hydrophobic
2 which promotes air entrapment between the substrate and
3 the aqueous environment.

4
5 Typically the surface chemistry of the formulation is
6 such that when coated on a substrate it can control the
7 surface tension between the fluid environment, the
8 formulation structure and a substrate.

9
10 The formulation can be attached to the substrate by
11 physical or chemical means or via a combination of
12 physical and chemical means. Substrates can include
13 resin composites, metal, wood, steel, aluminium,
14 concrete, natural rock, thermosetting plastic, and
15 rubber based substrates. These substrates can be pre-
16 treated with primers to help adhesion of the
17 microparticles. A typical primer coating would be an
18 epoxy based anti-corrosion primer used to prime mild
19 steel substrates.

20
21 Suitably the formulation can comprise of micro-
22 particles chosen from the group containing:

23
24 pyrogenic metal oxides such as fumed silica, fumed
25 alumina, fumed cesium, fumed zirconia, fumed
26 titania, fumed itrium, fumed chromium, fumed tin,
27 fumed molybdenum oxides and fumed vandium oxide;

28
29 carbon black or channel black pigment particles;

30
31 finely ground inorganic or organic particles such
32 as talc, mica, bentones, calcium carbonate, iron
33 and lead oxides; and

34
35 precipitated particles such as precipitated
36 silicon dioxide, silica, aluminium silicates and

1 titanium dioxides, silica based particles such as
2 hydrogels, solgels or aerogels, and synthetic
3 resin based particulate products such as
4 Pergopak.
5

6 Hydrophillic micro-particles, foams or micro-filaments
7 can also be used. These can be treated to create the
8 surface tension or hydrophobicity required to entrap
9 the gaseous phase between the substrate and the fluid
10 phase. Treatment can be done prior to, during or
11 after application to the substrate.
12

13 Suitably also, the formulation can comprise of porous
14 or semi-porous foams or membranes that could be created
15 using a polyurethane moisture curing resin that is
16 foamed and treated to create the required surface
17 tension or hydrophobicity to promote the gas or vapour
18 phase entrapment.
19

20 Suitably also, the formulation can comprise of micro-
21 filaments that mimic the behaviour of either bird
22 feathers or animal fur to entrap air. These micro-
23 filaments can be made from organic or inorganic
24 materials, such as glass or plastic.
25

26 Typically the surface energy of the structure of the
27 formulation may be adapted by controlling the
28 hydrophobicity of the structure. This can be done
29 prior to, during or after the application of the
30 coating or surface modification to the substrate.
31

32 Preferably the micro-particles, foam or micro-filaments
33 are treated with agents chosen from the group
34 comprising natural and synthetic waxes, siloxanes,
35 fluoro-silanes, reactive silanes, silicon oils, organo-
36 silanes, organo-titanate compounds, other silicon and

1 hydrocarbon based materials or blends of the above.
2 These treatments can occur during, prior to or after
3 the application of the coating or surface modification
4 to the substrate.

5
6 Suitable commercially available modified micro-
7 particles include Aerosil R202, Aerosil R974, Aerosil
8 R805, HDK H2000, Sypernat D10, Syloid ED 60, Neosyl and
9 Aerosil R504, Bayer Titan Products, Winofil, Bentones,
10 sementious clays, Laponites, Pergopack, Aluminium Oxide
11 C, Titanium Oxide P25, etc.

12
13 In one particular embodiment, the formulation comprises
14 of a dispersion of a treated fumed silica in a blend of
15 solvents, and/or water and/or additives. The additives
16 would be used to improve the performance of the coating
17 or surface modification. Such additives could be
18 catalysts, adhesion promoters, fungicides, hardener,
19 biocides, reactive silanes, surface tension modifiers
20 and corrosion inhibitors. The composition of the
21 solvent/water/additives dispersion could vary depending
22 on the choice of substrate. A dispersion of a treated
23 fumed silica in water and a range of similar additives
24 could also be used. This coating can be applied to a
25 partially or fully cured primer coating on a metal
26 substrate. A typical primer coating could be an epoxy
27 based coating.

28
29 In an alternative embodiment, the formulation comprises
30 use of a treated fumed silica blended with a hydro-
31 carbon resin wherein the hydro-carbon resin bonds the
32 silica to a substrate surface. Additives as described
33 above can also be used to improve the hydrophobic
34 performance of the coating or surface modification.

35
36 Preferably the fumed silica is prepared from highly

1 dispersed amorphous silicon dioxide treated with
2 dimethyldichlorosilane, hexamethyldisilazane or
3 polymethylsiloxane or composite hydrophobic treatments.

4
5 Preferably the bonding resin is an epoxy, a
6 polyurethane, a polyester, a vinylester, an acrylic or
7 composites of the above.

8
9 The bonding resin may be a powder or in a selected
10 solvent/resin solution. The microparticles can be
11 coated onto the substrate held in a solvent blend or
12 aqueous dispersion. The bonding of the microparticles
13 can be improved by further treating it with other
14 chemical compounds that aid adhesion by either
15 chemical, electrostatic or physical means. An example
16 of this could be treating a hydrophobic fumed silica
17 with an Amino Silane or an Organotitanate or blends to
18 improve chemical adhesion to an epoxy resin based
19 coated substrate. A commercial product would be
20 Aerosil R504.

21
22 Suitably the coating formulation comprises from 1% to
23 90% fumed, treated hydrophobic silica.

24
25 Suitably the coating formulation comprises from 1% to
26 90% hydro-carbon resin.

27
28 The formulation can also be applied directly to a
29 partially cured, uncured, pre-vulcanised, post-
30 vulcanized or thermosetting substrate. An example
31 would be passing a heated thermosetting plastic coated
32 wire through a bath of a dry silica or a dispersion
33 containing silica.

34
35 The invention further provides a process for coating a
36 substrate, the process comprising the steps of heating

1 the selected coating formulation to between 50°C -
2 300°C and depositing the composition on to the
3 substrate.

4
5 Alternatively, the invention provides a process for
6 coating a substrate, the process comprising the steps
7 of preheating the substrate and depositing the coating
8 formulation on to the substrate.

9
10 For hydro-carbon oil fluid systems oleophobic
11 treatments such as fluorine derivatives may be used to
12 entrap the required gas or vapour. These are of
13 specific value in oil/water systems. Similar delivery
14 and bonding mechanisms can be used as described
15 previously.

16
17 In an alternative embodiment of the invention, a
18 metallised coating may be used.

19
20 Amongst others, any or all of zinc, aluminium and
21 nickel metals may be used.

22
23 The invention further comprises a process for coating a
24 substrate with a metallised coating, the process
25 comprising heating a blend of fumed treated hydrophobic
26 silica and metal to between 100°C - 1000°C and
27 depositing the blended composition on the substrate.

28
29 Suitably a sand mill, pebble mill or steel ball
30 horizontal mill may be used to blend treated silica and
31 resin, metal, solvent blend or aqueous dispersion.

32
33 A coating formulation may be deposited by being sprayed
34 or painted onto the substrate.

35
36 Alternatively the composition may be electrostatically

1 deposited onto the substrate.

2

3 The choice of micro-particles, resin or metal and the
4 treatment will depend on the substrate to be coated,
5 the environment in which the substrate is to be
6 situated and the required properties in that
7 environment. An example of a formulation according to
8 the invention is now further described with reference
9 to Fig 1.

10

11 In the example shown in Fig 1, the treated fumed silica
12 is blended with the hydro-carbon resin wherein the
13 hydro-carbon resins bonds the silica to the substrate
14 surface.

15

16 The fumed silica in this example is the reaction
17 product of the flame hydrolysis of a silane compound
18 (typically a chloro or fluoro silane) which is further
19 treated with dimethyldichlorosilane,
20 hexamethyldisilazane or polymethylsiloxane. This
21 treatment imparts hydrophobicity to the fumed silica.
22 Superhydrophobicity, however, requires the synergy of
23 the silicon water repellent and the entrapment of air
24 or blends of the above with other silane materials.

25

26 This is illustrated in Fig 1. The hydro-carbon resin
27 forms a surface on the substrate with the hydrophobic
28 silica entrapping air between the substrate and the
29 water.

30

31 A coating such as this effectively prevents the
32 adhesion to a marine hull of the fouling bio-net
33 without the requirement of toxic compounds leaching
34 into the ocean, e.g. TBT, the treatment for anti-
35 fouling currently employed.

36

1 A further advantage in the use of the coating is the
2 reduction of hydrodynamic drag and the consequent fuel
3 economy.

4
5 Therefore, according to the present invention, there is
6 provided a coating formulation wherein the creation of
7 a micro layer of air or gas or vapour phase between the
8 substrate and aqueous or liquid phase results in
9 improved hydro-dynamic or co-efficient of friction
10 characteristics created between the aqueous or fluid
11 phase and the substrate. Also, the coating prevents
12 and controls the formation of a bio-net and has
13 negligible ecological impact in a marine environment.

14
15 The coating also provides reduced contact or prevention
16 of the contact of the substrate with the aqueous or
17 fluid phase. The coating further improves the
18 substrates overall chemical resistance to the fluid
19 phase. The micro-layer between the fluid and the
20 substrate will help reduce or prevent the osmosis of
21 the fluid occurring across or through the substrate.
22 An example of this would be the reduction or prevention
23 of the phenomenon known as "osmotic" blistering of
24 polyester constructed pleasure boat hulls.

25
26 The application of such a coating or surface
27 modification to a substrate could reduce the possible
28 formation of ice on the substrate. A typical
29 application of this would be to reduce the build up of
30 ice on an aeroplane wing.

31
32 Further modifications and applications may be made
33 without departing from the scope of the invention
34 herein intended.

35
36 /u/mur/specs/p18291-
37

1 CLAIMS

2

3 1. A formulation suitable for coating or modifying
4 the surface of a substrate to be situated in an
5 aqueous or fluid environment wherein the
6 formulation is capable of producing and/or
7 entrapping a micro layer of gas or vapour phase
8 between the substrate and the aqueous or fluid
9 environment.

10

11 2. A formulation as claimed in Claim 1 wherein the
12 entrapped gas is air.

13

14 3. A formulation as claimed in Claim 1 or Claim 2
15 which comprises of a structure of micro-particles.

16

17 4. A formulation as claimed in Claim 1 or Claim 2
18 which comprises of semi or semi-permeable foams or
19 membrane.

20

21 5. A formulation as claimed in Claim 1 or Claim 2
22 which comprises of micro filaments.

23

24 6. A formulation as claimed in any one of the
25 preceding Claims comprising a hydrophobic
26 structure.

27

28 7. A formulation as claimed in Claim 3 wherein the
29 micro-particles are chosen from the group
30 containing:

31

32 pyrogenic metal oxides such as fumed silica, fumed
33 alumina, fumed cesium, fumed zirconia, fumed
34 titania, fumed itrium, fumed chromium, fumed tin,
35 fumed molybdenum oxides and fumed vandium oxide;
36 carbon black or channel black pigment particles;

1 finely ground inorganic or organic particles such
2 as talc, mica, bentones, calcium carbonate, iron
3 and lead oxides; and

4
5 precipitated particles such as precipitated
6 silicon dioxide, silica, aluminium silicates and
7 titanium dioxides, silica based particles such as
8 hydrogels, solgels or aerogels, and synthetic
9 resin based particulate products such as
10 Pergopak.

11
12 8. A formulation as claimed in any one of the
13 preceding Claims treated with agents chosen from
14 the group comprising natural and synthetic waxes,
15 siloxanes, fluoro-silanes, reactive silanes,
16 silicon oils, organo-silanes, organo-titanate
17 compounds, other silicon and hydrocarbon based
18 materials or blends of the above.

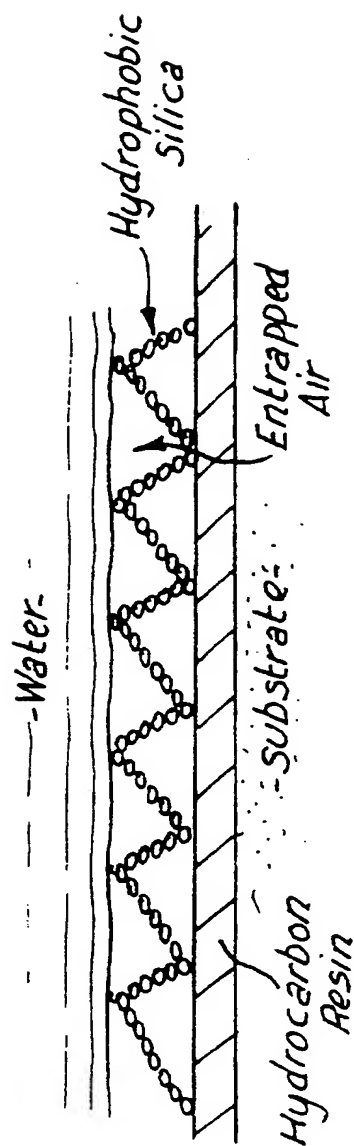
19
20 9. A process for coating a substrate, the process
21 comprising the steps of heating formulation as
22 claimed in any one of Claims 1 to 8 to between
23 50°C - 300°C and depositing the composition on to
24 the substrate.

25
26 10. A process for coating a substrate, the process
27 comprising the steps of preheating the substrate
28 and depositing a coating formulation on to the
29 substrate.

30
31 11. A process for coating a substrate with a
32 metallised coating, the process comprising heating
33 a blend of fumed treated hydrophobic silica and
34 metal to between 100°C - 1000°C and depositing the
35 blended composition on the substrate.

36

1/1

FIG. 1

INTERNATIONAL SEARCH REPORT

National Application No

GB 97/00349

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D5/16 B63B1/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09D B63B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 973 510 A (MCCULLOUGH ET AL) 10 August 1976 see column 1, line 66 - column 3, line 15; claims 1,3-5	1
A	EP 0 616 940 A (MITSUI ENGINEERING & SHIPBUILDING) 28 September 1994 see page 3, line 9 - page 4, line 20 see page 11, line 1 - line 49; claims 1,2,5,6	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

12 June 1997

Date of mailing of the international search report

25.06.97

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 97/00349

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3973510 A	10-08-76	NONE	
EP 616940 A	28-09-94	AU 4834393 A	26-04-94
		BR 9305682 A	03-12-96
		CN 1095030 A	16-11-94
		DE 69309655 D	15-05-97
		NO 941964 A	26-05-94
		US 5476056 A	19-12-95
		WO 9407740 A	14-04-94
		JP 7017476 A	20-01-95

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